Exceptional service in the national interest

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QMC Training Program: Using QMCPACK for condensed matter

Luke Shulenburger

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Questions answered by this lecture

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- How are calculations of solids different from isolated molecules?
- What are finite size effects and how are they mitigated?
- What are the current best practices for using pseudopotentials in condensed phases?

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COMPUTING THE INTERACTION ENERGY

Using a finite size simulation to approximate an infinite solid

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- Calculations of ever larger clusters are slow to converge to the bulk limit
- Periodic boundary conditions (PBC) significantly speed this convergence
- In moving to PBC, the coulomb potential between charged particles is replaced by a periodic Ewald potential

Ewald Sums

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- The periodic interaction is found by summing the interactions of an infinite array of periodic charges
  - This is only conditionally convergent for the coulomb interaction
- The standard procedure for computing these is to introduce a Gaussian screening of the charge and to perform part of the sum in real space and part in reciprocal space

$$V(r,r') = \sum_{i,j,k} \frac{qq'}{\left|r - r' + n_i a_i + n_j a_j + n_k a_k\right|} \rightarrow \sum_{r' \in I} \frac{qq'}{\left|r - r'\right|} \exp(\sqrt{\alpha}\left|r - r'\right|) + \frac{V}{2} \sum_k \frac{4\pi}{k^2} \left|\rho(k)\right|^2 \exp(-k^2 / 4\alpha)$$

Optimized Ewald sums

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- Qmcpack uses an optimized form of the Ewald interaction
  - Natoli and Ceperley. Journal of Computational Physics. **117**, 171 (1995)
  - Instead of screening the delta function charge with a gaussian and summing the compensating charge in reciprocal space, explore other choices of screening
  - The form of the screening is optimized so as to minimize the number of terms necessary in the resulting summations
  - The error in the method goes as $e^{-k_c r_c}$
    - The product of the cutoff values r_c and k_c is called LR_DIM_CUTOFF in the qmcpack input file

Why do we care so much

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- The real space part of the ewald sum has on the order of 100's to 1000's of terms, as does the reciprocal space part
  - Aren't flops free?
- How many times do we evaluate the interaction between point charges in a periodic DMC calculation?

Why do we care so much

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- The real space part of the ewald sum has on the order of 100's to 1000's of terms, as does the reciprocal space part
  - Aren't flops free?
- How many times do we evaluate the interaction between point charges in a periodic DMC calculation?
  - For each Monte Carlo sweep, propose moves of O(100) electrons
  - For each single particle move evaluate O(100) interactions
  - In a solid state calculation we typically have O(1000) walkers
  - The population is generally moved O(1000) times per simulation
    - The interaction is calculations on the order of 10^{10} times

Arbitrary boundary conditions

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- Purely periodic boundary conditions are a choice made for convenience in QMCPACK
- It is equally possible to mix boundary conditions
  - For example periodic in two directions and open in the third for a slab calculation
  - Ewald sums or their equivalent can be derived in a mix of boundary conditions
    - Compare this to plane wave DFT codes
  - The appropriate potentials are also implemented in QMCPACK

References

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- Optimized Ewald
  - Natoli and Ceperley. Journal of Computational Physics. **117**, 171 (1995)
- RMP on solids
  - Foulkes, Mitas, Needs and Rajagopal, RMP **73**, 33 (2001)

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BASIS SETS FOR REPRESENTING THE WAVEFUNCTION

Background

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- The simplest and most common wavefunction used in solid state calculations has a Slater-Jastrow form
- The Jastrow factors will be determined through optimization
- The single particle orbitals that go into the Slater determinant are calculated by another theory

Single particle orbitals for DMC

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- The most common source for single particle orbitals for solid state calculations is from a DFT code
- These wavefunctions are typically represented in a plane wave basis:

$$\phi_i(\vec{r}) = \sum_j c_{ij} e^{\vec{k}_j \cdot \vec{r}}$$

- Each single particle move requires evaluating every orbital at a new position
  - In a plane wave basis set, this means all N plane waves must be evaluated for every orbital!

Single particle orbitals for DMC

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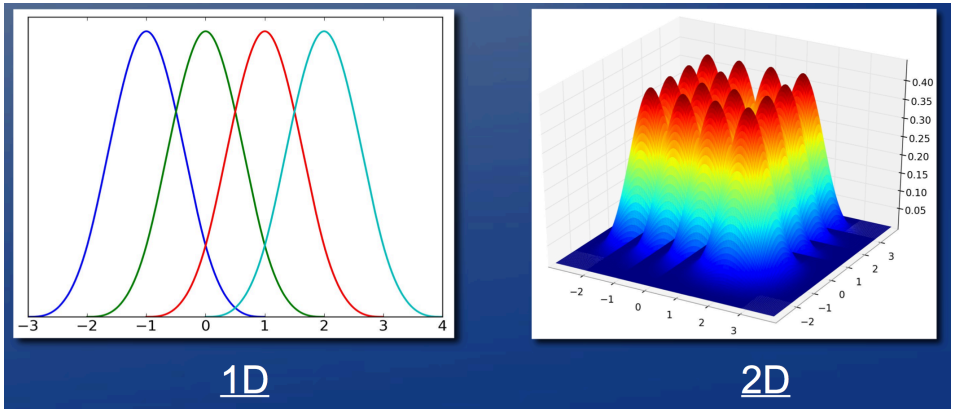
- Plane wave representations are inefficient
- A real space basis is much more efficient
  - Extensive testing shows that 3D b-splines are a good choice for efficiency
  - Only 64 basis elements are nonzero at each point (versus thousands or more for plane waves)
  - $B_{ijk}(x,y,z) = a_i(x)b_j(y)c_k(z)$



- Efficient routines exist to convert from a plane wave basis to b-splines with an arbitrary real space spacing using the FFT

B-splines and memory

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- QMCPACK uses a regularly spaced grid of points to calculate the 3d b-splines
  - Extremely efficient lookup in memory and streaming of many wavefunctions to CPU
  - Inefficient in terms of total memory used
    - All wavefunctions may be small in a region of space (for instance if vacuum is included in the calculation)
    - Wavefunctions typically vary most rapidly near nulcei
    - Some single-particle wavefunctions may be small in some regions but large in others

Memory usage and wavefunctions

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- QMCPACK can address several of these memory issues
  - If vacuum is included in the calculations, two sets of b-spline tables can be used
    - One coarse table valid everywhere
    - One fine table (factor of 2 smaller spacing between points) is used in a parallelpiped surrounding the atoms
    - Preserves efficient streaming of data from memory to the CPU
    - If half of the cell is vacuum, memory usage is reduced by a factor of 0.625

Memory usage and wavefunctions

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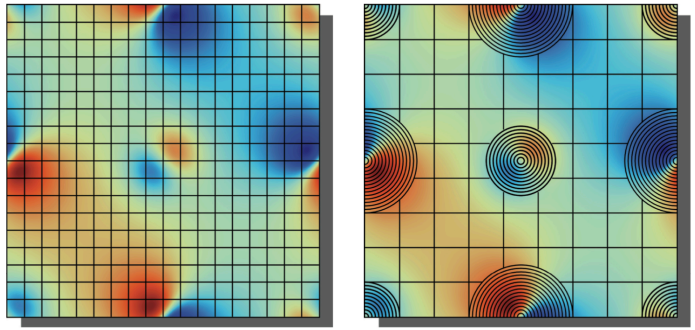
- QMCPACK can address several of these memory issues
  - If high plane wave cutoffs are necessary due to rapid wavefunction variations near the nucleus
    - Use a hybrid representation inspired by APW
      - Around each nucleus, the wavefunctions are represented as a radial spline times spherical harmonics



      - In the interstitials a coarse b-spline representation is used
      - The regular b-spline table is still kept for all space so as to ease memory access
      - The memory used is often reduced by a factor of 4-8

Memory usage and wavefunctions

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- Not implemented is the capability to localize wavefunctions in real space and truncate the orbitals
  - In the case of insulators, localized Wannier functions can be constructed
  - If the orbitals can be truncated, it is possible to reduce the complexity of the wavefunction evaluation
    - For a given point in space, the number of nonzero orbitals depends only on the local environment, not on the total number of electrons
    - Williamson, Hood and Grossman, PRL **87**, 246406 (2001)

Additional memory saving trick

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- In the case of highly symmetric systems, another trick can be used
  - For orbitals coming from a mean field theory, use Bloch's theorem to construct wavefunctions in a supercell from wavefunctions in the primitive cell
  - This reduces memory usage by a factor of N where N is the number of copies of the primitive cell.

QMCPACK Hybrid Parallelism and memory

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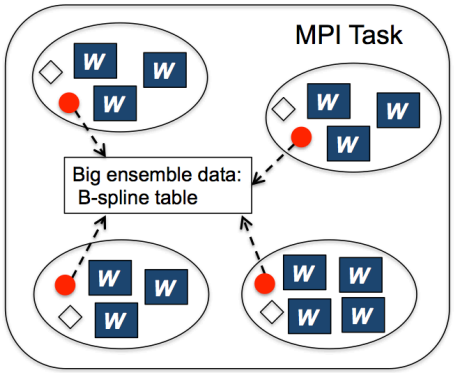
- Moves for a given walker are evaluated by a single processing unit (CPU core)
  - So every core has to be able to quickly evaluate all single particle wavefunctions at all points in space
  - Modern supercomputers typically have 10s of cores per node
  - The single particle wavefunctions are never changed during the calculations
  - Share them between all of the cores on a node
- QMCPACK uses a combination of MPI and OpenMP for parallelzation
  - OpenMP on a node makes sharing large static data for the wavefunciton easy
- Reduces required memory by nearly a factor of the number of cores per node



References

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- Splines in qmc
  - Alfe and Gillan, PRB **70**, 161101(R) (2004)
- Linear scaling qmc
  - Williamson, Hood and Grossman, PRL **87**, 246406 (2001)
- GPU paper (APW trick)
  - Esler et al. CiSE **14**, 40 (2012)
- Hybrid parallelization in QMCPACK
  - Kim et al. J. Phys: Conference Series **402**, 012008 (2012)

Questions

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- How does memory usage increase when doubling the supercell size?
- More…

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FINITE SIZE EFFECTS

Origin of finite size effects

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- Periodic boundary conditions imply that the Hamiltonian is unchanged upon discrete translations of the system
  - The single particle wavefunctions can pick up an arbitrary phase at the boundary: (Bloch Theorem)

  - Must integrate over all such boundary conditions
    - Brillouin zone integration (k-points) in DFT
    - Twist averaging in QMC

$$\Psi(\vec{r}+\vec{T}) = e^{i\vec{k}\cdot\vec{T}}\Psi(\vec{r})$$

Twist Averaging in DMC

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- Twist averaging refers to averaging over boundary conditions
  - Choosing the phase of the boundary conditions is equivalent to applying a magnetic field

$$H = \frac{\left(p + \frac{e}{c}A(R)\right)^2}{2m} + \sum_{i>j} \frac{e^2}{|r_i - r_j|}$$

  - Splitting into real and imaginary parts:

$$H|\Phi(R)| = \left[\sum_{i=1}^{N} \frac{p_i^2}{2} + V(R)\right]|\Phi(R)| = E|\Phi(R)|$$

$$\sum_{i=1}^{N} \nabla_i \left\{|\Phi(R)|^2 \left[\nabla_i \varphi(R) + A(r_i)\right]\right\} = 0$$

Twist Averaging in DMC

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- With an imaginary part of the wavefunction it becomes less clear how to apply the fixed node approximation

- The fixed phase approximation uses choice for the phase and then solves the real part of the equations using what looks like fixed node DMC

Twist Averaging in practice

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- There is a relationship between the one body finite size effects in DMC and the integration over k-points in DFT
  - Their effects should be the same in the case that both theories find the same fermi liquid parameters
  - In some cases the approximation that DFT with N k-points has the same 1-body finite size effect as DMC with N twists is quite accurate
  - DMC calculations at different twist angles are statistically independent, so the cost of twist averaging is negligible except for initialization and equilibration

Twist Averaging in practice

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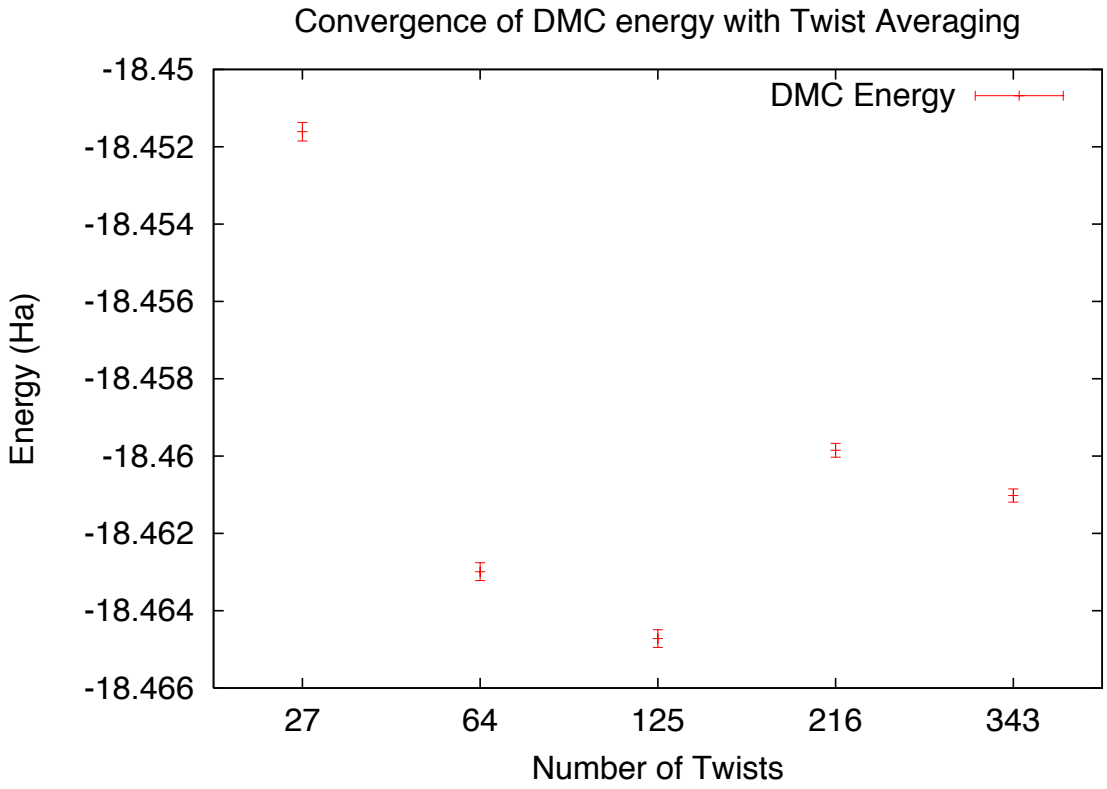
- Using 1-8 twists is often not enough, especially for metals
- Symmetry can be used to reduce the number of calculations
  - Especially useful if operating in a massively parallel fashion



Two body finite size effects

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- Arise from the interaction of each charged electron with an infinite lattice of the electrons
  - The pair correlation function acquires a spurious structure at large distances
- For supercells of the same aspect ratio, error in the energy per particle goes as 1/N where N is the number of particles in the system
- Extrapolation to infinite system size is typically very expensive
  - Requires 3 different cell sizes

Finite Size Correction Schemes

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- Approximate methods exist to correct the total energy for these finite size effects
  - Only total energies are currently available
- Three methods are in wide use
  - Approximate DFT Functional
  - Replacing the Coulomb interaction
  - Fit to the long range behavior from the RPA

Finite size corrections: Approximate functional

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- Based on work of Kwee, Zhang and Krakauer. PRL 100, 126404 (2008)
- Notice that widely used solid state DFT functionals contain correlation from the electron gas extrapolated to the thermodynamic limit
- Create family of DFT functionals parameterized on the energy of the electron gas including finite size errors
  - Use this functional to calculate total energy within DFT and compare to standard functional
    - $\Delta DFT^{FS} = E(\infty)-E^{FS}(L)$
    - $\Delta DFT^{2B} = E(L)-E^{FS}(L)$
- Best chance of accuracy when DFT is already doing a good job of describing the system
  - Not the most exciting place to spend millions of CPU hours on DMC…

Finite size corrections: Effective interaction

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- Introduce an effective interaction that accounts for the hartree energy exactly, but the exchange-correlation energy is evaluated using 1/r

$$V_{MPC} = \frac{1}{2}\sum_{i\neq j} f(r_i - r_j) + \sum_i \int_\Omega \rho(r)[V_e(r_i - r) - f(r_i - r)]dr - \frac{1}{2}\int_\Omega \rho(r)\rho(r')[V_e(r - r') - f(r - r')]dr\,dr'$$

  - Requires knowledge of the charge density (usually obtained from an auxiliary method like DFT)
  - The cost of evaluating the interaction does not grow with system size
  - Can be quite accurate, but misses the part of the finite size effect due to the change in kinetic energy

Finite size corrections: Fit to RPA

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- The electron-electron interaction energy can be written as

$$V = \frac{e^2}{4\pi^2}\int \frac{S(k)-1}{k^2}dk$$

- In a finite simulation cell, the structure factor may only be sampled at k vectors commensurate with the supercell, so

$$V_N = \frac{2\pi e^2}{\Omega}\sum_{k\neq 0}\frac{S_N(k)-1}{k^2}$$

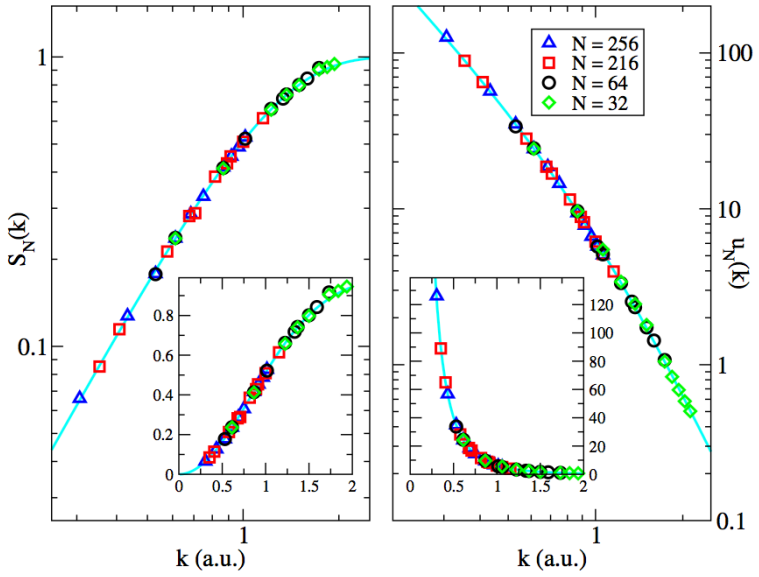
- The finite size error in the total energy comes from the difference between these expressions

Finite size corrections: Fit to RPA

- The dominant error in those terms comes from small k
  - S(k) for k->0 is known from the RPA
  - Fit calculated S(k) to RPA form: $\hbar k^2/2m\omega_p$
  - Correction is due to the difference between the integral and the sum for small k
- A similar procedure works for the kinetic energy where

$$\Delta T_N = \frac{\hbar^2}{4m(2\pi)^3}\int dk k^2 u(k) - \frac{\hbar^2}{4m\Omega}\sum_{k\neq 0} k^2 u_N(k)$$

- This relies on the fact that the calculated structure factor and jastrow factor do not change greatly when working in finite size supercells



Silicon structure factor and jastrow factor from Chiesa et al. PRL 97, 076404 (2006)

References

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- Twist Averaging
  - Lin, Zong and Ceperley, PRE 64, 016702 (2001)
  - Ortiz, Ceperley, Martin, PRL 71, 2777 (1993)
- Approximate Functional
  - Kwee, Zhang, Krakauer, PRL 100, 126404 (2008)
- Model Interaction
  - Fraser et al. PRB 53, 1814 (1996)
  - Kent et al. PRB 59, 1917 (1999)
  - Williamson et al. PRB 55, R4851 (1997)
- Fit to RPA
  - Chiesa et al. PRL 97, 076404 (2006)

Questions

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- How do finite size effects in DMC differ from those in DFT?
- More…

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PSEUDOPOTENTIALS

Pseudopotentials

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- While the cost of DMC scales approximately as N^3 with the number of electrons, scaling with Z is considerably worse
  - N^3 factor due to number of electrons per ion
  - Increasing energy scale decreases the approximate error in the trial wavefunction, increasing the variance
  - The timestep must also be reduced
  - Estimates place the cost at $Z^{5.5\text{-}6.5}$

Pseudopotentials

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- The obvious solution to this problem is to introduce pseudopotentials (an effective potential that represents the core) and only simulate the valence electrons
  - In most theories these are nonlocal objects (different potentials for different angular momenta)
    - How to introduce a nonlocal potential in DMC?

Pseudopotentials

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- First approach is the locality approximation
  - Mitas, Shirley and Ceperley, J. Chem. Phys 95, 3467 (1991)
  - For a given nonlocal potential, use the effective interaction of that potential on the trial wavefunction as a local potential in the DMC

$$H_{eff} = K + V_{loc} + \frac{\int dx' \langle x' | V_{nonloc} | x \rangle \Psi_T(x')}{\Psi_T(x)}$$

    - This is exact when the trial wavefunction is exact
    - This is NOT variational
  - The approximation is only applied to the nonlocal parts of the potential treated in a semilocal form

Pseudopotentials

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- More on the form of pseudopotentials we can handle
- Must be a semi-local pseudopotential

$$V = V_{loc}(r) + \sum_{lm} \left|Y_{lm}\right\rangle v_l(r) \left\langle Y_{lm}\right|$$

- More modern forms of the potential involving projectors, eg

$$V = V_{loc}(r) + \sum_{lm} \frac{\left|\delta V_l \phi_{lm}\right\rangle \left\langle \delta V_l \phi_{lm}\right|}{\left\langle \phi_{lm}\right| \delta V \left|\phi_{lm}\right\rangle}$$

  - Are not tractable because of the difficulty of evaluating the projectors within DMC
- Techniques like nonlinear core corrections are similarly not possible to use

Pseudopotentials

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- The variational principle can be restored for evaluating nonlocal pseudopotentials
  - Casula, PRB 74, 161102(R) (2006)
- Introduce a discrete version of the Green's function which can be sampled
- Known colloquially as t-moves
- This technique is also more numerically stable than the locality approximation when the nonlocal potential is large
- This has been observed to have a somewhat larger timestep error than the locality approximation

Pseudopotentials

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- Have so far focused on mechanics (how to apply a pseudopotential)
- What makes a good pseudopotential?
  - Acioli and Ceperley, J. Chem. Phys. 100, 8169 (1994)
  - The all electron and pseudo one body density matrices should agree beyond the core radius
  - Make the natural orbitals agree beyond the core radius

Pseudopotentials

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- Most pseudopotentials used do not come from correlated calculations
  - Popular forms come from DFT or Hartree Fock
- It is important to have a smooth behavior of the potential at the origin
- The hardness of the pseudopotential is not particularly important except that the trial wavefunction from the DFT will be larger
  - However, potentials with smaller nonlocal components will result in less error due to the locality approximation
- Be careful that in solid state calculations modern DFT codes almost always use the Kleinman-Bylander form
  - QMC will use semilocal, so there is a potential mismatch

Questions

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- What calculations can be used to validate a pseudopotential for use in DMC?

References

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- Locality approximation
  - Mitas, Shirley and Ceperley, J. Chem. Phys 95, 3467 (1991)
- T-moves
  - Casula, PRB 74, 161102(R) (2006)
- Many body pseudopotential theory
  - Acioli and Ceperley, J. Chem. Phys. 100, 8169 (1994)
- Pseudopotential libraries
  - Trail-Needs: http://vallico.net/casinoqmc/pplib/
  - BFD: http://www.burkatzki.com/pseudos/index.2.html

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MISCELLANEOUS

How to reduce the fixed node error?

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- Direct optimization of the single particle wavefunctions is generally not feasible
  - In a plane wave basis set there are thousands of coefficients per single particle orbital
    - Much easier of using a compact representation such as gaussians
- Trial wavefunctions beyond single slater-Jastrow
  - Multi-determinant expansions converge very slowly and are not size consistent at a given level of truncation
  - Inhomogeneous backflow transformations are possible but are often very expensive
    - Also, unless cutoff of the transformation is very small, single particle moves are inefficient

Excitations

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- Band structure
  - The fixed node approximation allows for excited states to be calculated if the nodal surface enforces orthogonality with the ground state
    - Particle-hole excitations satisfy this
  - Extended Koopmans theorem is also possible
    - See Kent et al. PRB, **57**, 15293 (1998)
  - Another possibility is correlation function Monte Carlo

References

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- Inhomogeneous backflow
  - Lopez-Rios et al, PRE **74**, 066701 (2006)
- Extended Koopmans's Theorem
  - Kent et al, PRB **57**, 15293 (1998)
- Correlation Function Monte Carlo
  - Ceperley and Bernu, J. Chem. Phys **89**, 6316 (1988)
- Wavefunction optimization for excited states
  - Schautz and Filippi, J. Chem. Phys **120**, 10931 (2004)

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QMC IN CONDENSED MATTER IN PRACTICE

QMC in condensed matter in practice

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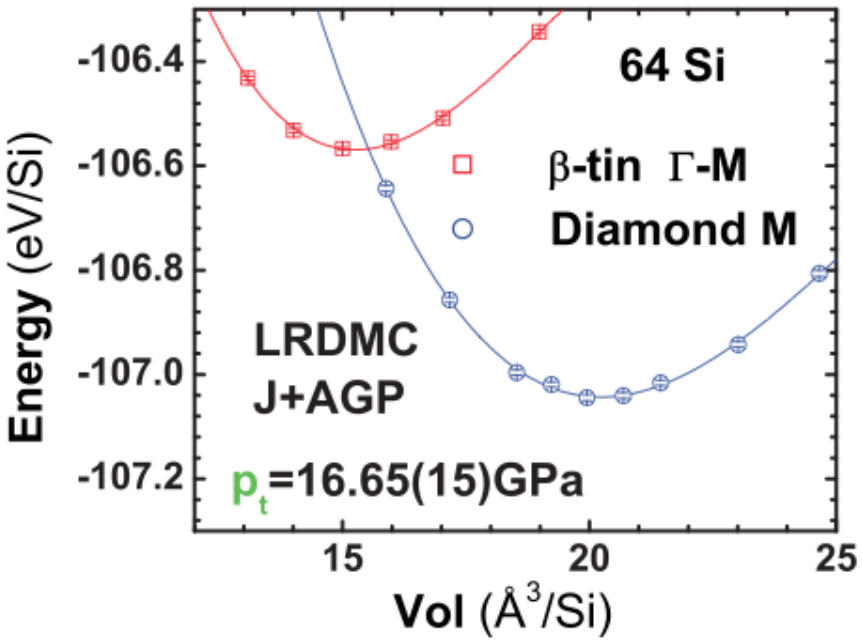
- Calculations of condensed phases involve a variety of approximations
  - Most approximations may be made arbitrarily small, but approaches to this are not standardized
- Finite size effects
  - One body effects -> DFT comparison or twist averaging
  - Two body effects -> Extrapolation, KZK functional or MPC / Chiesa combination
- Fixed node errors
  - Slater jastrow wavefunction, self healing, backflow, geminals, pfaffians, multideterminants
- Pseudopotentials
  - Only valence electrons simulated because of computational cost
  - In which approximation should core and valence be separated
  - Correction via all electron calculation or comparison with all electron DFT

Approximation methods can greatly affect results

- Case study on Si
- Total energies of diamond and beta-Sn phases calculated with DMC / LRDMC
- Quasiharmonic phonon corrections included



Method	Raw (GPa)	Corrected (GPa) ($T = 300$ K)
LDA	7.21	6.34
PBE	9.87	8.99
VMC	15.48 ± 0.06	13.3 ± 1.0
LRDMC	16.65 ± 0.15	14.5 ± 1.0
DMC (Ref. 18)	19.0 ± 0.5	16.5 ± 0.5
DMC (Ref. 13)	16.5 ± 1.0	14.0 ± 1.0
AFQMC (Ref. 20)	15.1 ± 0.3	12.6 ± 0.3
Expt.	$10.0 - 12.5$	$10.0 - 12.5$

Sorella et al. PRB 83, 075119 (2011)

Test approximations on a suite of solids

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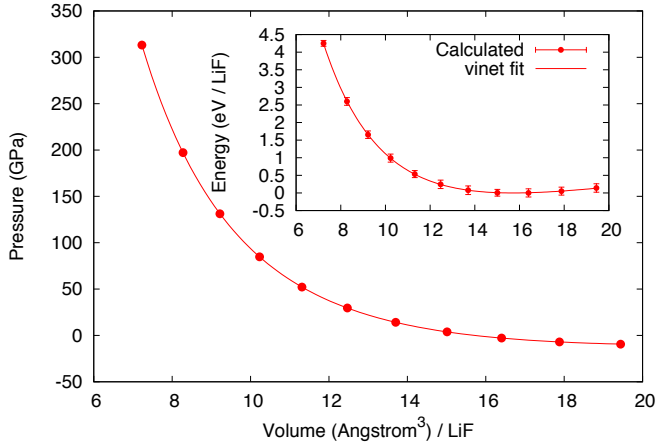
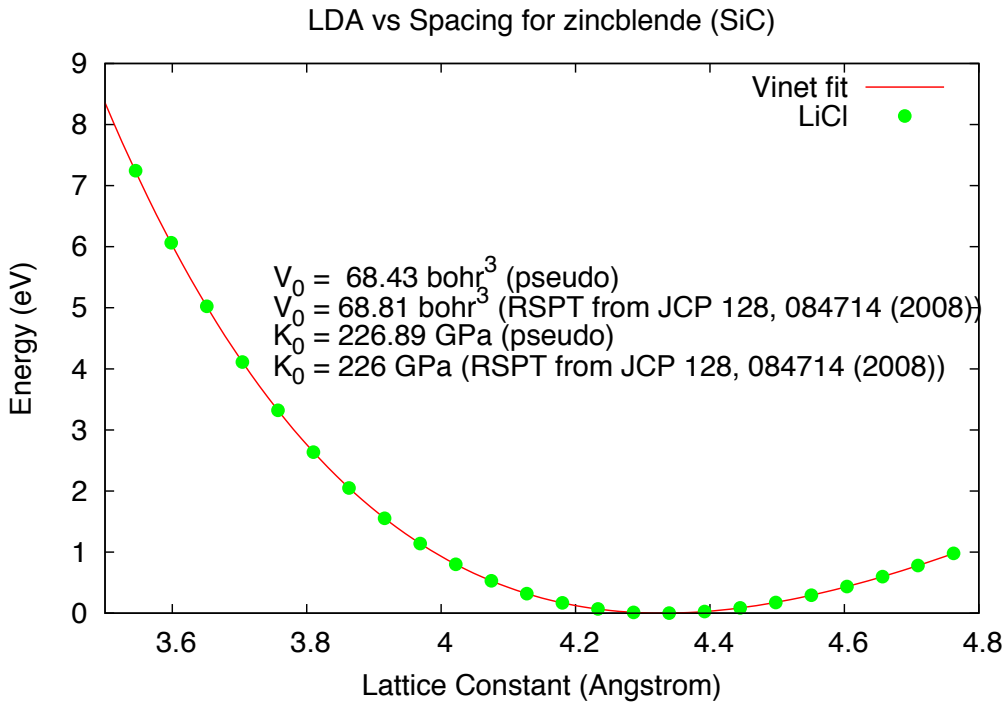
- Binding is different
  - Far less effect from degenerate energy levels at highest energy states
  - More effect from relative energy levels
- Test should compare to easily measured experimental data
  - high pressure calculations to derive properties of ambient phase
- Mitigate costs due to finite size convergence by comparing only within the same phase
- Previous calculations have required 1 year of time on NSF machines for a single solid
- Calculations performed on Cielo



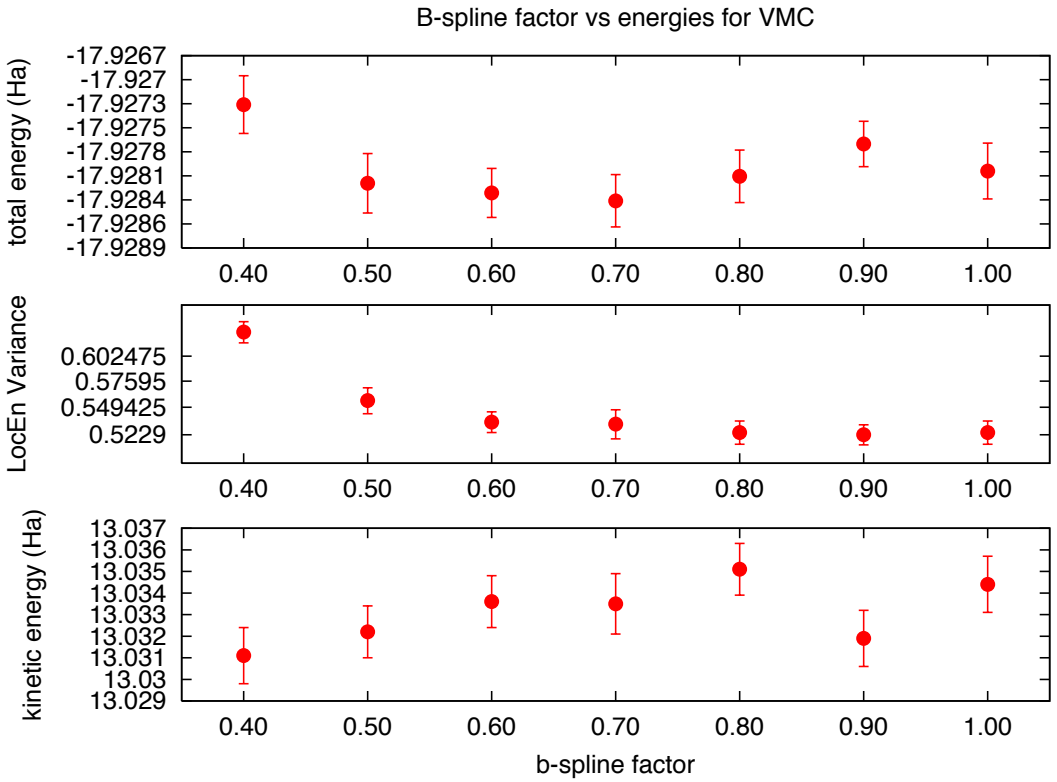
Pseudopotential Details

- LDA pseudopotentials constructed with OPIUM
- Compared to either LAPW calculations with elk or LMTO calculations with RSPT (Mattsson et al. JCP 128, 084714 (2008))
- Bulk modulus and equilibrium volume nearly same to minimize corrections such as applied in Maezono et al. PRB 82, 184108 (2010)



Convergence of technical parameters

- Tests performed for moderate size supercell at 2 volumes
- Time step, b-spline spacing and twist averaging converged to within meV
- Finite size convergence achieved when change to larger supercell produced same energy shift in ambient and high pressure calculations



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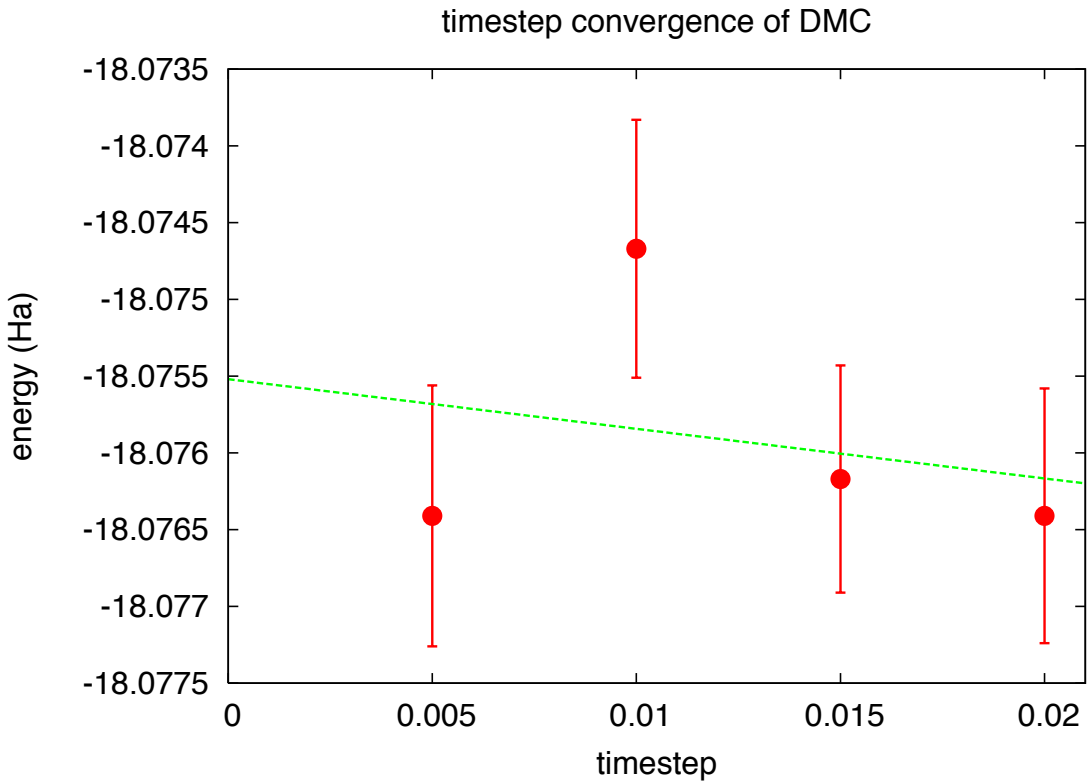

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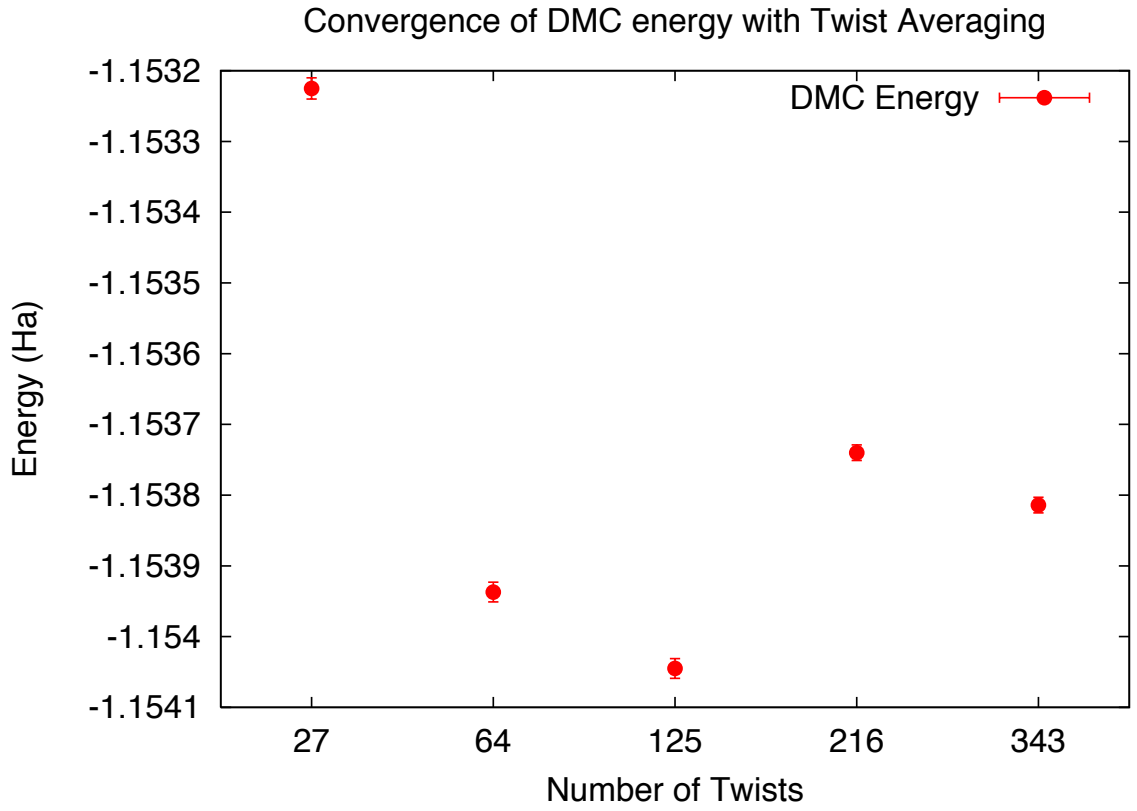

First ever extensive benchmarks of Quantum Monte Carlo for condensed matter

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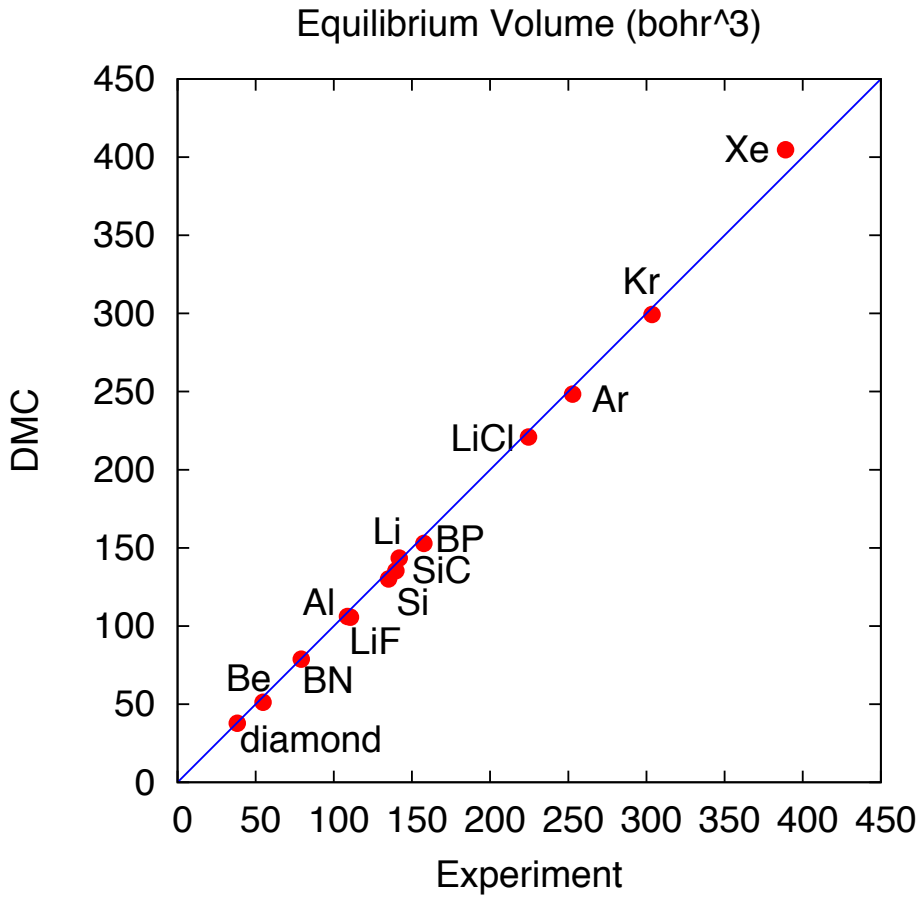
- Fit Vinet form to E(V) and compare equilibrium volume (density) and bulk modulus (compressibility) to experiment

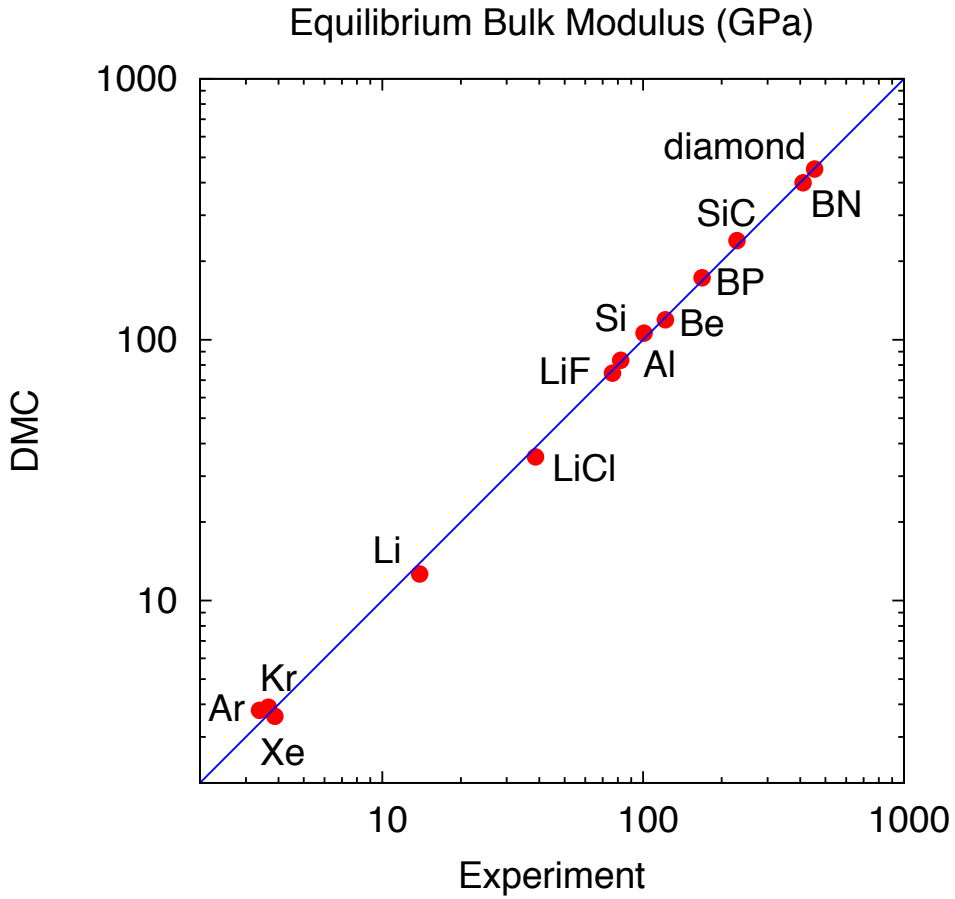


- Materials span a factor of 10 in equilibrium volume
- Four types of bonding are included
  - Ionic
  - Covalent
  - Metallic
  - Van der Waals
- Lattice Constants within ~0.9%
- This provides a new baseline procedure for a QMC calculations

Mean error: -0.38 +/- 0.15
Mean absolute error: 2.28 +/- 0.15
RMS error: -0.697 +/- 0.066%
Mean absolute relative error: 1.79 +/- 0.07%

First ever extensive benchmarks of Quantum Monte Carlo for condensed matter

- Fit Vinet form to E(V) and compare equilibrium volume (density) and bulk modulus (compressibility) to experiment

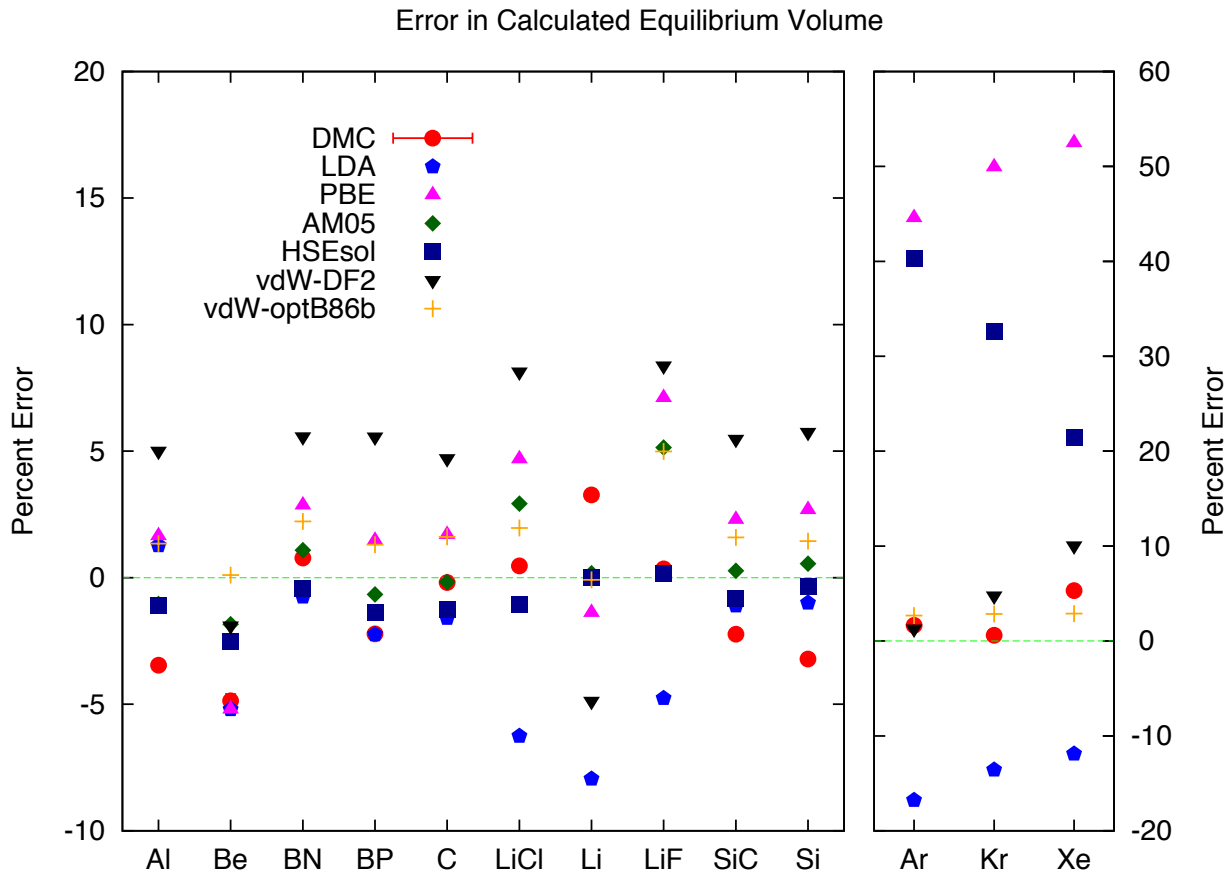


- Bulk modulus spans over 3 orders of magnitude
- This provides a new baseline procedure for a QMC calculations

Mean error: -0.07 +/- 0.42
Mean absolute error: 3.53 +/- 0.42
RMS error: 0.62 +/- 0.44%
Mean absolute relative error: 4.49 +/- 0.44%

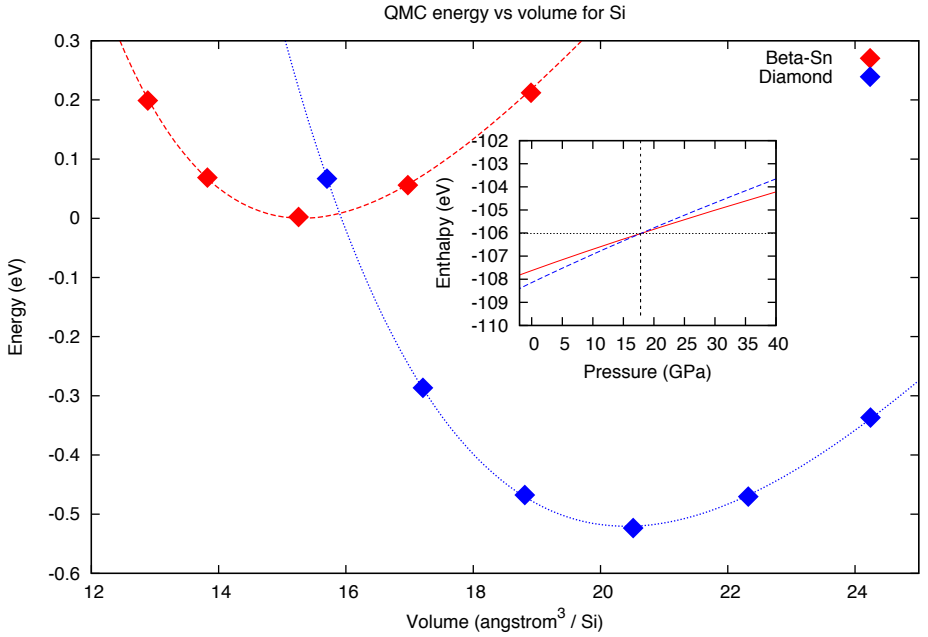
Compare to DFT functionals

- Compare to various "good" DFT functionals
  - LDA
  - PBE
  - AM05
  - HSEsol
  - vdW-DF2
  - vdW-optB86b
- Non van der Waals functionals yield high quality results on many materials
  - But not noble gases
- van der Waals functionals are improving to wide applicability



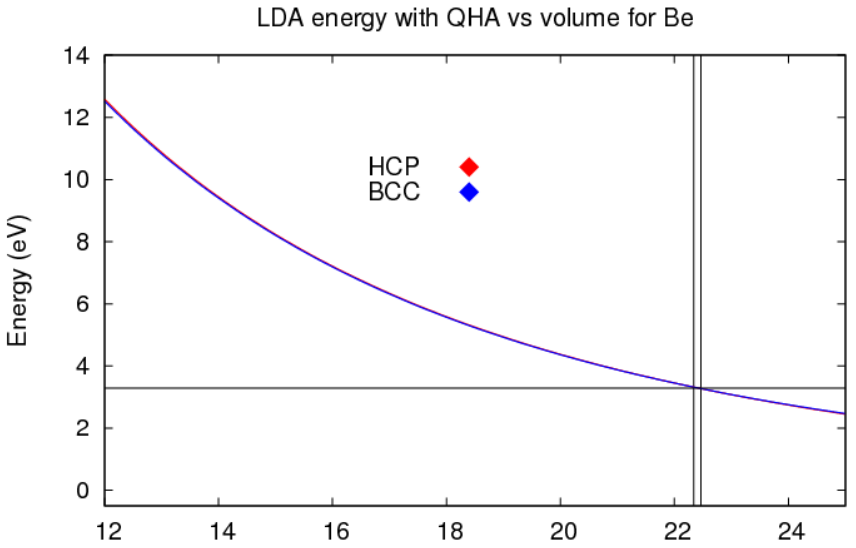
Si Phase transition revisited:
Utilizing methodology from benchmark fares little better

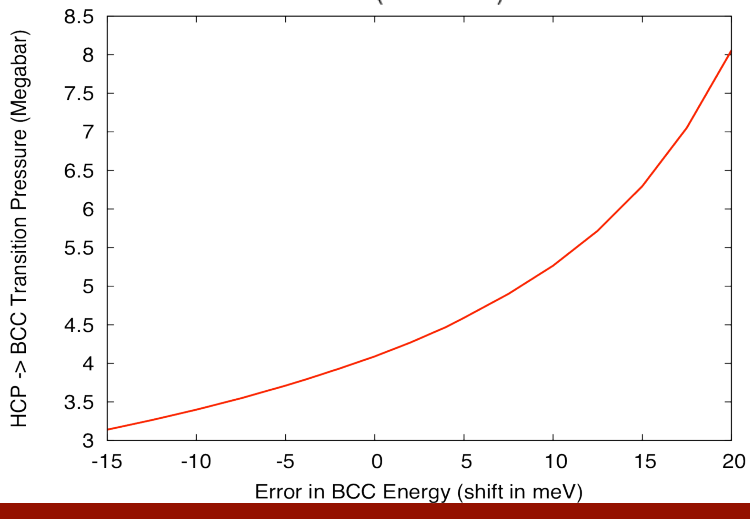
- Use DFT based pseudopotential
- Extensive twist averaging for Fermi surface
- Chiesa correction for kinetic energy and MPC for potential
- Equilibrium properties are worse than reported by other groups
  - **Equilibrium density 2% too small**
  - **Bulk Modulus 5% too large**
- Phase Transition pressure
  - **17.8 GPa (5-7.8 GPa too large!)**



See if this problem can be diagnosed in a simpler system

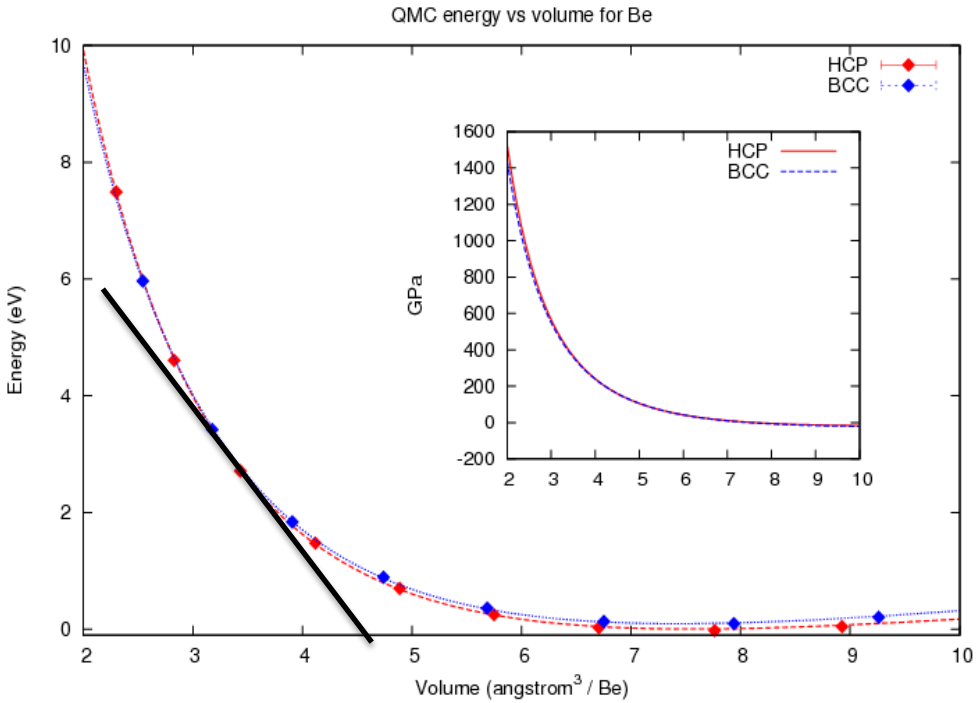
- Calculate Be HCP-> BCC phase transition pressure with LDA+QHA
- What is sensitivity of transition?
  - Make constant shift of $E_{BCC}(V)$
    - Transition pressure changes from 350 GPa to 525 GPa with a 1 kcal/mol shift
    - Zero point energies were an order of magnitude larger
- "Chemical Accuracy" is not good enough!





Early DMC calculations yielded disappointing results

- **Equation of state is fit using Vinet form**
  - More crucial because values have statistical errors
- **Phase transition occurs at > 700 GPa**
  - Significantly higher than DFT result ~ 390 GPa



HCP Equilibrium Parameters		
	QMC	Exp
c/a	1.569 +/- 0.004	1.568
V_0 (angstrom^3)	7.746 +/- 0.078	8.117
Bulk Modulus (Gpa)	124 +/- 2	116.8

All electron method significantly improves HCP phase description

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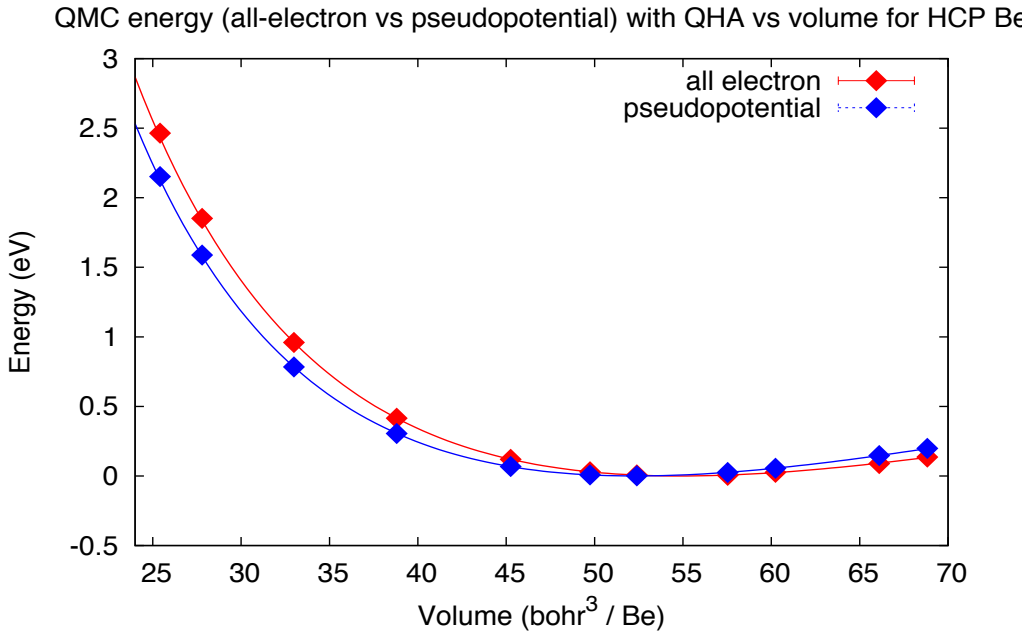
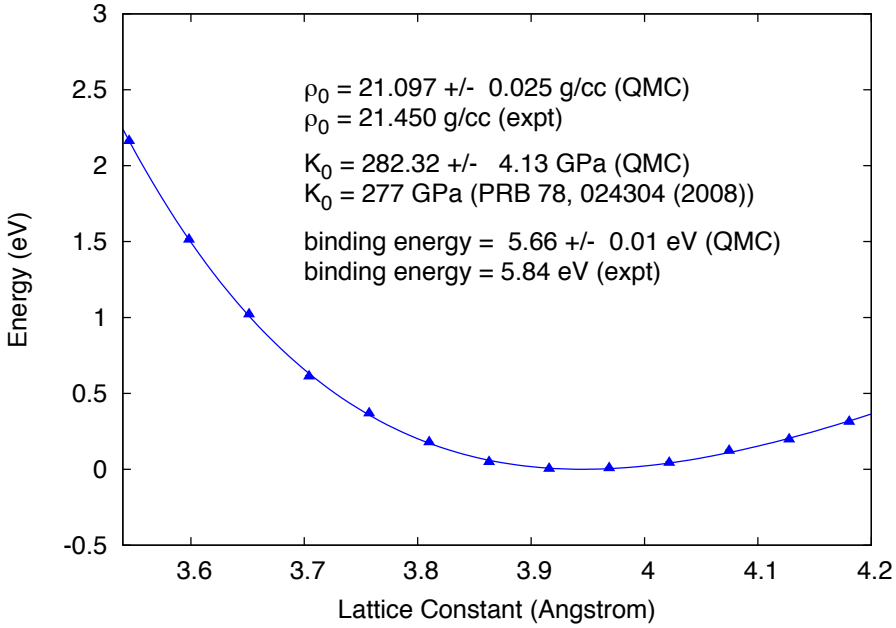


All EOS Properties agree with experiment within small error bars!

HCP Equilibrium Parameters			
	QMC	All Electron QMC	Exp
c/a	1.569 +/- 0.004	1.569 +/- 0.004	1.568
V_0 (angstrom^3)	7.746 +/- 0.078	8.129 +/- 0.012	8.117
Bulk Modulus (Gpa)	124 +/- 2	115.7 +/- 1.5	116.8

Revise pseudopotential generation scheme and apply to heavier elements

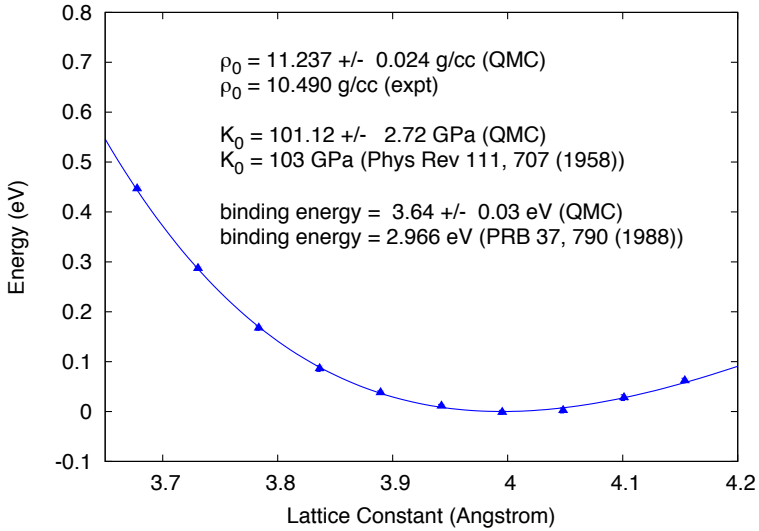
- Still require DFT based pseudopotentials to accurately reproduce all electron results
- Attempt to reduce size of locality error by making nonlocal channels similar to local
- Preserve Kleinman-Bylander form for DFT, but allow change of local channel for DMC
- Choose core-valence separation based on separation in energy



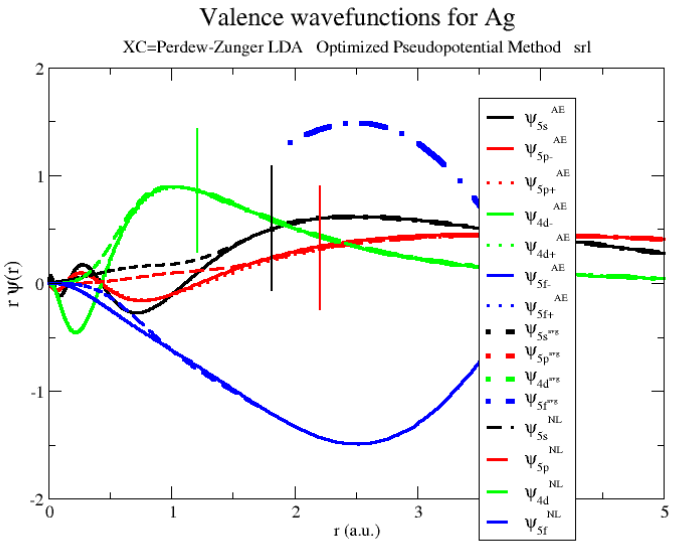
Application to FCC platinum yields encouraging results for ambient density, bulk modulus and cohesive energy

Unfortunately this method does not appear to be a silver bullet

- Elastic properties well reproduced
- Ambient density off by ~7%
- Variance of energy and timestep error are small
  - Wavefunction appears to be well matched to pseudopotential



- Consider strong spatial overlap of 4d with 5s and 5p wavefunctions



Efficient tests of pseudopotentials are helping to refine our experience

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- Calculate the ionization potential and electron affinity of atoms
- Calculate the binding curve of dimers
- Compare to experimental results
- Highly successful application in $CaCuO_3$ – Foyevtsova et al, PRX **4**, 031003 (2014)
- Many more elements becoming available